

CLAIMS

We Claim:

1. A method for preparing crosslinked particles, comprising:
  - (a) providing synthetic polymer molecules having a plurality of crosslinkable groups that are inert until activated, but which when activated undergo an irreversible intramolecular crosslinking reaction; and
  - (b) activating the crosslinkable groups under crosslinking conditions, whereby irreversible intramolecular crosslinking of the polymer molecules occurs to form crosslinked particles.
2. The method of Claim 1 wherein the crosslinked particles are inert under said crosslinking conditions with respect to intermolecular crosslinking with said polymer molecules.
3. The method of Claim 1 wherein the crosslinked particles are inert under said crosslinking conditions with respect to intermolecular crosslinking with each other.
4. The method of Claim 1 wherein the polymer molecules are added to a solvent prior to activation of the crosslinkable groups to form a polymer molecule solution, such that the crosslinkable groups are activated in the solvent and the crosslinked particles are formed therein.
5. The method of Claim 4 wherein (b) is carried out by slowly adding a coupling agent to the polymer molecule solution so as to promote intramolecular crosslinking.
6. The method of Claim 1 wherein the crosslinkable groups are thermally activatable, and (b) is carried out by heating the polymer molecule.
7. The method of Claim 6 wherein (b) is carried out by adding the polymer molecules to a solvent maintained at a temperature sufficiently high to activate the crosslinkable groups.
8. The method of Claim 1 wherein the crosslinkable groups are photolytically activatable, and (b) is carried out by irradiating the polymer molecule.

- 1 9. The method of Claim 1 wherein the crosslinkable groups are activatable with  
2 ultraviolet radiation, ionizing radiation, or electron beam radiation.
- 1 10. The method of Claim 9 wherein (b) is carried out by slowly adding the polymer  
2 molecules to an irradiated solvent so as to promote intramolecular crosslinking.
- 1 11. The method of Claim 1 wherein the crosslinkable groups are activatable by a  
2 chemical activating agent, and (b) is carried out by contacting the polymer  
3 molecules with the chemical activating agent.
- 1 12. The method of Claim 11 wherein (b) is carried out by slowly adding the chemical  
2 activating agent to the polymer molecules so as to facilitate intramolecular  
3 crosslinking.
- 1 13. The method of Claim 11 wherein (b) is carried out by slowly adding the polymer  
2 molecules to the chemical activating agent so as to facilitate intramolecular  
3 crosslinking.
- 1 14. The method of Claim 11 wherein the chemical activating agent is selected from  
2 the group consisting of free radical initiators, acids, bases, organic catalysts,  
3 organometallic catalysts, metallic catalysts, nucleophiles and electrophiles.
- 1 15. The method of Claim 1 wherein the molecular weight of the polymer molecules is  
2 selected to provide crosslinked particles approximately 2 nm to 100 nm in  
3 diameter.
- 1 16. The method of Claim 15 wherein the molecular weight of the polymer molecules  
2 is selected to provide crosslinked particles approximately 2 nm to 25 nm in  
3 diameter.
- 1 17. The method of Claim 16 wherein the molecular weight of the polymer molecules  
2 is selected to provide crosslinked particles approximately 2 nm to 10 nm in  
3 diameter.
- 1 18. The method of Claim 1 wherein the number of crosslinkable groups on the  
2 polymer molecules is selected to provide a crosslinked particle approximately 2  
3 nm to 100 nm in diameter.
- 1 19. The method of Claim 18 wherein the number of crosslinkable groups on the

- 2 polymer molecules is selected to provide a crosslinked particle approximately 2  
3 nm to 25 nm in diameter.
- 1 20. The method of Claim 19 wherein the number of crosslinkable groups on the  
2 polymer molecules is selected to provide a crosslinked particle approximately 2  
3 nm to 10 nm in diameter.
- 1 21. The method of Claim 1 wherein the crosslinking density on the polymer  
2 molecules is selected to provide a crosslinked particle approximately 2 nm to 100  
3 nm in diameter.
- 1 22. The method of Claim 21 wherein the crosslinking density on the polymer  
2 molecules is selected to provide a crosslinked particle approximately 2 nm to 25  
3 nm in diameter.
- 1 23. The method of Claim 22 wherein the crosslinking density on the polymer  
2 molecules is selected to provide a crosslinked particle approximately 2 nm to 10  
3 nm in diameter.
- 1 24. The method of Claim 4 wherein the polymer molecules and the crosslinkable  
2 groups thereon are selected so that the hydrodynamic volume of the crosslinked  
3 particles in the solvent is up to about 80% less than the hydrodynamic volume of  
4 the polymer molecules prior to crosslinking.
- 1 25. The method of Claim 24 wherein the hydrodynamic volume is about 5-60% less  
2 than the hydrodynamic volume of the polymer molecules prior to crosslinking.
- 1 26. The method of Claim 25 wherein the hydrodynamic volume is about 35-50% less  
2 than the hydrodynamic volume of the polymer molecules prior to crosslinking.
- 1 27. The method of Claim 25 wherein the hydrodynamic volume is about 5-30% less  
2 than the hydrodynamic volume of the polymer molecules prior to crosslinking.
- 1 28. The method of Claim 1 wherein the polymer molecules are linear.
- 1 29. The method of Claim 1 wherein the polymer molecules are branched.
- 1 30. The method of Claim 29 wherein the polymer molecules are star polymers,  
2 hyperbranched polymers, graft polymers or dendritic polymers.
- 1 31. The method of Claim 1 wherein the polymer molecules are block copolymers and

- 2 the crosslinkable groups are contained in at least one block of the polymer  
3 molecule.
- 1 32. The method of Claim 1 wherein the polymer molecules have a backbone  
2 comprised of monomer units selected from the group consisting of ethylenically  
3 unsaturated polymerizable monomers, nitrogenous polymers, olefins,  
4 condensation monomers, ring-opening monomers, esters, sulfones, lactides,  
5 lactones, carbonates, imides, arylenes, amides, propylene, ethers, urethanes, vinyl  
6 and vinyl derivatives, and organic polysilicas.
- 1 33. The method of Claim 32 wherein each crosslinkable group is directly bound to a  
2 monomer unit.
- 1 34. The method of Claim 32 wherein each crosslinkable group is indirectly bound to a  
2 monomer unit through a linking group.
- 1 35. The method of Claim 1 wherein the crosslinkable groups are selected from the  
2 group consisting of acryloyl, lower alkyl-substituted acryloyl, vinyl, substituted  
3 vinyl, cyclic ether, cyclic ester, activated ester, cycloalkenyl, acid halide, amino,  
4 alcohol, phenol, carboxylic acid, diacetylene, unsubstituted and substituted  
5 acetylene groups, eonophiles, dienophiles and substituted and unsubstituted  
6 bicyclo[4.2.0]octa-1,3,5-trienyl groups.
- 1 36. The method of Claim 1 wherein the crosslinked particles are randomly formed.
- 1 37. The method of Claim 1 wherein the polymer molecules further comprise a  
2 chemical moiety.
- 1 38. The method of Claim 37 wherein the chemical moiety is a pharmaceutical agent,  
2 catalyst, functional group, surfactant, sensor group or photoresponsive unit.
- 1 39. The method of Claim 1 wherein (b) is conducted in the presence of a chemical  
2 moiety whereby the chemical moiety is incorporated into the crosslinked particle.
- 1 40. The method of Claim 39 wherein the crosslinked particle has at least one  
2 functional group on its backbone and wherein the chemical moiety is attached to  
3 the crosslinked particle at said functional group.
- 1 41. The method of Claim 40 wherein the chemical moiety is a pharmaceutical agent,

catalyst, functional group, surfactant, sensor group or photoresponsive unit.

42. The method of Claim 1, which further comprises incorporating the crosslinked particles into a matrix.

43. The method of Claim 42 wherein the decomposition temperature of the crosslinked particles is less than the decomposition temperature of the matrix, and the method further comprises heating the matrix to the decomposition temperature of the crosslinked particles, whereby the crosslinked particles decompose to create a porous matrix.

44. A method for preparing crosslinked particles, comprising:

(a) providing synthetic polymer molecules having a plurality of crosslinkable groups that are inert until activated, but which when activated undergo an irreversible intramolecular crosslinking reaction; and

(b) activating the crosslinkable groups under conditions effective to promote said intramolecular crosslinking reaction, such that crosslinked particles are formed; and wherein the conditions in (b) are effective to substantially prevent intermolecular crosslinking between the polymer molecules, such that (b) results in formation of a single crosslinked particle from a single corresponding polymer molecule.

45. The method of Claim 44 wherein less than 10% of the polymer molecules participate in intermolecular crosslinking.

46. The method of Claim 45 wherein less than 5% of the polymer molecules participate in intermolecular crosslinking.

47. The method of Claim 44 wherein the crosslinkable groups are thermally activatable; photolytically activatable; activatable with ultraviolet radiation, ionizing radiation, or electron beam radiation; or activatable by a chemical activating agent.

48. The method of Claim 44 wherein the polymer molecules have a backbone comprised of monomer units selected from the group consisting of ethylenically unsaturated polymerizable monomers, nitrogenous polymers, olefins,

condensation monomers, ring-opening monomers, esters, sulfones, lactides, lactones, carbonates, imides, arylenes, amides, propylene, ethers, urethanes, vinyl and vinyl derivatives, and organic polysilicas.

49. The method of Claim 44 wherein the crosslinkable groups are selected from the group consisting of acryloyl, lower alkyl-substituted acryloyl, vinyl, substituted vinyl, cyclic ether, cyclic ester, activated ester, cycloalkenyl, acid halide, amino, alcohol, phenol, carboxylic acid, diacetylene, unsubstituted and substituted acetylene groups, eonophiles, dienophiles and substituted and unsubstituted bicyclo[4.2.0]octa-1,3,5-trienyl groups.

50. The method of Claim 44 wherein the crosslinked particles are randomly formed.

51. The method of Claim 44 which further comprises incorporating the crosslinked particles into a matrix.

52. The method of Claim 51 wherein the decomposition temperature of the crosslinked particles is less than the decomposition temperature of the matrix, and the method further comprises heating the matrix to the decomposition temperature of the crosslinked particles, whereby the crosslinked particles decompose to create a porous matrix.

53. A method for preparing crosslinked particles in a solvent, comprising:

(a) providing synthetic polymer molecules having a plurality of crosslinkable groups that are inert until activated, but which when activated undergo an irreversible intramolecular crosslinking reaction to form a crosslinked particle;

(b) activating the crosslinkable groups; and

(c) adding the synthetic polymer molecules to a solvent under conditions effective to allow said irreversible intramolecular crosslinking reaction to take place while substantially preventing intermolecular reaction, resulting in formation of a single crosslinked particle from a corresponding polymer molecule in said solvent.

54. The method of Claim 53 wherein (b) is carried out prior to (c).

- 1 55. The method of Claim 53 wherein (b) is carried out during or subsequent to (c).
- 1 56. The method of Claim 53 comprising repeating (a), (b) and (c) without diluting the  
2 solvent or removing crosslinked particles therefrom.
- 1 57. The method of Claim 53 wherein in (a), the synthetic polymer molecules are  
2 provided in solution.
- 1 58. The method of Claim 57 wherein the conditions comprise providing the solution  
2 at a sufficiently dilute concentration so as to substantially prevent intermolecular  
3 reactions following activation of the crosslinking groups.
- 1 59. The method of Claim 53 wherein the conditions comprise adding the synthetic  
2 polymer molecules to the solvent slowly so as to substantially prevent  
3 intermolecular crosslinking between the polymer molecules relative to the rate at  
4 which the intramolecular crosslinking reaction occurs.
- 1 60. The method of Claim 53 wherein the conditions comprise adding the solution of  
2 the synthetic polymer molecules to the solvent slowly so as to substantially  
3 prevent intermolecular crosslinking between the polymer molecules.
- 1 61. The method of Claim 53 wherein the solvent is selected from the group consisting  
2 of benzyl ether; N-cyclohexylpyrrolidinone; N-methylpyrrolidone;  
3 dimethylacetamide; dimethylphenyl urea; N,N-dimethyltrimethylene urea; butyl  
4 acetate; 2-ethoxyethanol; cyclopentanone; cyclohexanone;  $\gamma$ -butyrolactone;  
5 lactate esters; ethoxyethylpropionate; alkylene glycol alkyl ether esters; alkylene  
6 glycol alkyl ethers; alkylene glycol monoalkyl esters; butyl acetate; 2-  
7 ethoxyethanol; ethyl 3-ethoxypropionate; polyethylene glycols and alkyl and aryl  
8 derivatives; diphenyl ether; diphenyl sulfone; ethylene carbonate; and mixtures  
9 thereof.
- 1 62. The method of Claim 53 wherein the crosslinkable groups are thermally  
2 activatable, and the solvent is at a temperature sufficiently high to activate the  
3 crosslinkable groups.
- 1 63. The method of Claim 53 which further comprises incorporating the crosslinked  
2 particles into a matrix.

- 1 64. The method of Claim 63 wherein the decomposition temperature of the  
2 crosslinked particles is less than the decomposition temperature of the matrix, and  
3 the method further comprises heating the matrix to the decomposition temperature  
4 of the crosslinked particles, whereby the crosslinked particles decompose to  
5 create a porous matrix.
- 1 65. A method for preparing a porous dielectric material, comprising:  
2 (a) providing synthetic polymer molecules having a plurality of  
3 crosslinkable groups that are inert until activated, but which when activated  
4 undergo an irreversible intramolecular crosslinking reaction;  
5 (b) activating the crosslinkable groups under crosslinking conditions,  
6 whereby irreversible intramolecular crosslinking of the polymer molecules occurs  
7 to form crosslinked particles;  
8 (c) mixing the crosslinked particles with a host matrix material to form  
9 a mixture, wherein the decomposition temperature of the crosslinked particles is  
10 less than the decomposition temperature of the host matrix material; and  
11 (d) heating the mixture to the decomposition temperature of the  
12 crosslinked particles, so that the crosslinked particles decompose to create a  
13 porous dielectric material.
- 1 66. The method of Claim 65 which has closed cell pores having a diameter of about  
2 2- 25 nm.
- 1 67. A method for forming an integrated circuit comprising:  
2 (a) positioning, on a substrate, a layer of a mixture of crosslinked  
3 particles having diameters less than about 25 nm and a host matrix material,  
4 wherein the decomposition temperature of the crosslinked particles is less than the  
5 decomposition temperature of the host matrix material;  
6 (b) heating the mixture to the decomposition temperature of the  
7 crosslinked particles to decompose the crosslinked particles and create a porous  
8 dielectric layer;  
9 (c) lithographically patterning the dielectric layer;



- 10 (d) depositing a metallic film on the patterned dielectric layer; and  
11 (e) planarizing the film to form an integrated circuit.
- 1 68. A porous dielectric matrix comprised of an organic material and having closed  
2 cell pores whose diameters fall substantially in the range of 2-25 nm.
- 1 69. The matrix of Claim 68 which has closed cell pores whose diameters fall  
2 substantially in the range of 2-10 nm.
- 1 70. The matrix of Claim 68 wherein the organic material is a polyphenylene oligomer  
2 or polymer.
- 1 71. An integrated circuit comprising a patterned dielectric layer and a planarized  
2 metallic film, wherein the dielectric matrix is comprised of an organic material  
3 and having closed cell pores whose diameters fall substantially in the range of 2-  
4 25 nm.
- 1 72. The integrated circuit of Claim 71 wherein the matrix has closed cell pores whose  
2 diameters fall substantially in the range of 2-10 nm.
- 1 73. The integrated circuit of Claim 72 wherein the organic material is a  
2 polyphenylene oligomer or polymer.